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For: CHEMICAL IMAGING OF A LITHOGRAPHIC PRINTING PLATE

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Substitute Specification
(Preliminary Amendment)

1

2 **CHEMICAL IMAGING OF A LITHOGRAPHIC PRINTING PLATE**

3 **CROSS REFERENCE TO RELATED APPLICATIONS**

4 This application is a divisional of U.S. Application Serial No. 10/057,152, filed October
5 25, 2001, which is, in turn, a continuation-in-part of U.S. Application Serial Nos. 09/941,304 and
6 09/941,323, both filed August 29, 2001, which are, in turn, divisionals of U.S. Application Serial
7 No. 09/566,455, filed May 8, 2000. This application also claims benefit of U.S. Provisional
8 Application Serial Nos. 60/281,742, 60/281,743 and 60/281,744, all filed on April 3, 2001.

9

10 **BACKGROUND OF THE INVENTION**

11 This invention relates to a process for imaging a lithographic printing plate and more
12 particularly to a process using an ink jet printer to imagewise apply an insolubilizing chemical to
13 a plate coating which comprises photosensitive compounds or their reaction products.

14 In the art of lithographic printing it is generally required that one or more lithographic
15 printing plates be mounted on a printing press. The lithographic printing plate is characterized by
16 having on its printing surface oleophilic ink receiving areas in the form of the image to be
17 printed, and hydrophilic water receiving areas corresponding to the other, non-printing areas of
18 the surface. Because of the immiscibility of oil-based lithographic inks and water, on a well-
19 prepared printing plate, ink will fully coat the oleophilic areas of the plate printing surface and
20 not contaminate the hydrophilic areas. The operating press brings the inked plate surface into
21 intimate contact with an impression cylinder or elastic transfer blanket that transfers the ink
22 image to the media to be printed.

1 Traditionally, a lithographic plate is photographically imaged. The plate substrate is most
2 commonly aluminum, from 5 to 12 mils thick, treated so that the printing surface is hydrophilic,
3 although treated or untreated plastic or paper substrates can also be used. The substrate is coated
4 with a solution of a photosensitive composition that is generally oleophilic. Upon drying, the
5 coating layer thickness is commonly about 1 to 3 microns thick. A printing plate with such a
6 photosensitive coating is called "presensitized" (PS). Both negative and positive working
7 photosensitive compositions are used in PS lithographic plates. In a negative plate, light
8 exposure insolubilizes the coating, so that on development the only parts of the coating that
9 aren't removed are the light imaged areas. The reverse is the case in a positive plate. Light
10 exposure solubilizes the coating; on development the coating is only removed in the areas that
11 are light imaged. In an image reversal process, a positive plate is "blanket exposed" or "flood
12 exposed", i.e., the entire plate is light exposed without any intervening mask or other means for
13 imaging, and imaged in a separate step which can be performed before or after the blanket
14 exposure step. By this image reversal process, a positive plate can be negatively imaged. The
15 aluminum substrate can be treated to make it hydrophilic either prior to the application of the
16 photosensitive composition or at the time the non-image areas of the coating are removed in a
17 development step. Such a process in which a pre-coated lithographic plate is prepared for press
18 by removing exclusively either the imaged or non-imaged coating in a development step is called
19 a subtractive process; a pre-coated plate having a coating which is at least partially removed in a
20 development step is known as a subtractive plate.

21 Photosensitive compositions used in positive lithographic plates are well known. They are
22 comprised primarily of alkali soluble resins and o-quinone diazide sulfonic acid esters or amides.

1 In addition dyes or colored pigments, indicator dyes, plasticizers and surfactants can also be
2 present. The ingredients are typically dissolved in organic solvents and are coated onto the
3 substrate. Upon drying a thin film or coating is produced.

4 Alkali soluble resins useful in positive plates are well known and include phenol-
5 formaldehyde resins, cresol-formaldehyde resins, styrene-maleic anhydride copolymers, alkyl
6 vinyl ether-maleic anhydride copolymers, co-or ter-polymers that contain either acrylic or
7 methacrylic acids and poly(vinyl phenol). U.S. Pat. No. 4,642,282 describes an alkali soluble
8 polycondensation product that is also useful as the resin component in positive plates.

9 The o-quinone diazide compounds include o-benzoquinone diazides, o-naphthoquinone
10 diazides and o-anthraquinone diazides. O-quinone diazide compounds useful in positive plates
11 are well known and are described in detail in Light Sensitive Systems by J. Kosar, p.339-352.
12 They are further described in U.S. Pat. Nos. 3,046,118; 3,046,119; 3,046,120; 3,046,121;
13 3,046,122; 3,046,123; 3,148,983; 3,181,461; 3,211,553; 3,635,709; 3,711,285 and 4,639,406
14 incorporated in entirety herein by reference.

15 Such positive plates are sensitive to light in the wavelength range of from about 290 to
16 500nm. When used in the standard manner, photo-exposure causes the alkali insoluble o-
17 quinone diazide of the positive plate to be converted into an alkali soluble carboxylic acid. Upon
18 subsequent treatment with a developer, which is a dilute aqueous alkaline solution, the exposed
19 parts of the coating are removed. The unexposed coating is alkali insoluble, because the o-
20 quinone diazide is unaffected by the developer, and remains on the substrate.

21 Traditionally, lithographic plates are imaged by photographic transfer from original
22 artwork. This process is labor-intensive and costly. Hence with the advent of the computer

1 engendering a revolution in the graphics design process preparatory to printing, there have been
2 extensive efforts to pattern printing plates, in particular lithographic printing plates, directly using
3 a computer-controlled apparatus called a platesetter that is supplied with digital data
4 corresponding to the image to be printed. A platesetter has the capability to supply an image
5 forming agent, typically light energy or one or more chemicals, to a plate according to various
6 patterns or images as defined by digital data, i.e., to imagewise apply an image forming agent.
7 Specially manufactured lithographic plates may be required for certain types of platesetters.
8 Such a combination of a computer-controlled platesetter and the proprietary plates used with
9 them along with developer solutions and any other materials or apparatuses necessary to prepare
10 the plates for printing is known as a computer-to-plate (CTP) system.

11 Heretofore, many of the new CTP systems have been large, complex, and expensive.
12 They are designed for use by large printing companies as a means to streamline the prepress
13 process of their printing operations and to take advantage of the rapid exchange and response to
14 the digital information of graphic designs provided by their customers. Many of the new CTP
15 systems use light sources, typically lasers, to directly image PS plates. But using lasers to image
16 plates is very expensive, because the per-unit cost of the lasers is high and because they require
17 sophisticated focusing optics and electronic controls. If because of the cost only a single laser is
18 used, then time becomes a constraint because of the necessity of raster scanning. There remains
19 a strong need for an economical and efficient CTP system for the many smaller printers who
20 utilize lithographic printing.

21 In recent years, ink jet printers have replaced laser printers as the most popular hard copy
22 output printers for computers. Ink jet printers have several competitive advantages over laser

1 printers. One advantage is that it is possible to manufacture an array of 10's or even 100's of ink
2 jet nozzles spaced very closely together in a single inexpensive print head. This nozzle array
3 manufacturing capability enables fast printing ink jet devices to be manufactured at a much lower
4 cost than laser printers requiring arrays of lasers. And the precision with which such a nozzle
5 array can be manufactured and the jetting reliability of the incorporated nozzles means that these
6 arrays can be used to print high quality images comparable to photo or laser imaging techniques.
7 Ink jet printers also are increasingly being used for prepress proofing and other graphic arts
8 applications requiring very high quality hard copy output.

9 In spite of the large and rapidly growing installed base of ink jet printers for hard copy
10 output, ink jet printing technology is not commonly used in CTP systems. There are many
11 challenging technical requirements facing the practitioner who would design such an ink jet
12 based CTP system as can be seen in the prior art. A first requirement is that the ink jet ink used
13 to image the printing plate be jettable, able to form ink drops of repeatable volume and in an
14 unvarying direction. Further, for practical commercial application, the ink must have a long shelf
15 life, in excess of one year or more. US Pat. No. 5,970,873 (DeBoer et al) describes the jetting of
16 a mixture of a sol precursor in a liquid to a suitably prepared printing substrate. But any ink
17 constituents of limited solubility will render unlikely the practical formulation of a jettable, shelf-
18 stable ink. Similar problems exist in US Pat. No. 5,820,932 (Hallman et al) in which complex
19 organic resins are jetted, and US Pat. No. 5,738,013 (Kellet) in which marginally stable transition
20 metal complexes are jetted. In US Pat. No. 6,187,380 B1 (Hallman et al) and 6,131,514
21 (Simons), inks comprising acrylic resins such as trimethylolpropanetriacrylate and poly(ethylene-
22 co-acrylic acid, sodium salt), are jetted. While it may be possible to make such a ink formulation

1 work for the purposes of a short term experiment, it would almost certainly clog the nozzles of an
2 ink jet printhead were the ink allowed to remain in the printer for the weeks or more that would
3 be a requirement of practical commercial use.

4 Another requirement is that to be of wide utility, the ink jet based CTP system should be
5 able to prepare printing plates with small printing dots, approximately 75 microns in diameter or
6 smaller, so that high resolution images can be printed. Ink jet printers can produce such small
7 dots, but of those having substantial commercial acceptance, only ink jet printers employing
8 aqueous-based inks are practically capable of printing such small dots. Thus the systems
9 described in US Pat. Nos. 4,003,312 (Gunther), 5,495,803 (Gerber), 6,104,931 (Fromson et al),
10 and 6,019,045 (Kato) which use solvent-based hot melt inks will not allow the preparation of the
11 high resolution printing plates necessary for printed images of high quality. Further, hot melt
12 type inks typically freeze on top of the imaged media rather than penetrate into it. This would
13 prevent intimate mixing between potential reactants in the inks and corresponding potential
14 reactants in a PS plate coating. It is also required that the prepared printing plates be rugged,
15 capable of sustaining press runs of many thousands of impressions. The waxes used in the hot
16 melt inks described in US Pat. No. 6,019,045 (Kato) and 4833486 (Zerillo) would wear out in
17 such a long press run.

18 Another requirement of a successful ink jet based CTP system is that a mature plate
19 technology is to be preferred. Although the prior art demonstrates that it is not obvious to do so,
20 it greatly simplifies the development of an ink jet CTP system to be able to use commercially
21 available, widely accepted PS plates. There are many tradeoffs in the manufacture of
22 commercially practical lithographic plates. They must be highly sensitive to the imaging process

1 and yet thermally stable, stable in high humidity storage environments and yellow light, resistant
2 to fingerprints, of minimal toxicity and environmentally benign, easily developed in that small
3 dots are quantitatively resolved without dot blooming using developers that are of minimal
4 toxicity and environmentally benign, able to sustain long press runs, manufacturable at a low cost
5 per square foot, and many other practical requirements. US Pat. No. 5,695,908 (Furukawa)
6 describes a process for preparing a printing plate comprising a new plate coating containing a
7 water-soluble polymer that becomes water-insoluble in contact with a metal ion in a solution
8 jetted imagewise. But such a new plate coating is unlikely to meet the wide array of constraints
9 on a successful plate technology. U.S. Pat. No. 5,466,653 (Ma et al) describes a plate coating
10 that requires an impractically high reaction temperature for imaging. US Pat. No. 6,025,022
11 (Matzinger) describes a new plate coating on a glass substrate that would be unlikely to find wide
12 acceptance.

13 To use an ink jet printer in a positive imaging process is impractical because in typical
14 printing, the area of a plate containing images such as text, graphics, and line work, is much less
15 than the non-image containing area of the plate. Thus to be able to image widely accepted
16 positive plates with a negative imaging ink jet process is a unique, surprising, and valuable result.

17 Positive plates based on o-naphthoquinone diazide sulfonic acid esters can be modified
18 by the incorporation of alkaline materials to obtain image reversal. US Patent No. 4,104,070
19 describes the use of imidazolines; US Patent No. 4,196,003 describes the addition of secondary
20 and tertiary amines and US Patent No. 4,356,254 describes the addition of basic carbonium dyes
21 to produce image reversal. The sequential steps for this image reversal process are imagewise
22 light exposure, heat treatment, blanket light exposure and alkaline development. Those coatings

1 have never achieved any commercial success, which is attributed to the adverse effect on the
2 properties of the coating by the addition of the alkaline materials. US Patent No. 4,007,047
3 describes image reversal of a positive resist by a modification of the photoimaging process.
4 After imagewise exposure, the resist coating is subjected to an acid treatment by immersion into
5 a heated acid solution, which after a water rinse and drying steps produces a negative image after
6 blanket light exposure and development.

7

8 **SUMMARY OF THE INVENTION**

9 The present invention provides a process for preparing PS lithographic plates for printing by
10 employing an ink jet printhead to imagewise apply an insolubilizing chemical. In one aspect of
11 the invention, the steps comprise:

12 (a) providing an on-press developable PS plate;
13 (b) imagewise applying an insolubilizing chemical to the plate coating;
14 (c) heating the plate;
15 (d) mounting the plate on a printing press; and
16 (e) operating the press.

17 In another aspect of the invention, the steps comprise:

18 (a) providing a positive plate;
19 (b) blanket exposing the plate;
20 (c) imagewise applying an insolubilizing chemical to the plate coating;
21 (d) heating the plate; and
22 (e) developing the plate.

- 1 In yet another aspect of the invention, the steps comprise:
 - 2 (a) providing a plate with a coating;
 - 3 (b) imagewise applying an insolubilizing chemical to the coating;
 - 4 (c) heating the plate; and
 - 5 (d) washing the plate with a developing solution.

6 Accordingly, there are several objects and advantages of the present invention. An object
7 of the present invention is that it is easily embodied in a practical, reliable, and inexpensive ink-
8 jet-based CTP system with minimal constraints on the formulation of the imaging fluid, and in
9 that widely-available, commercially-accepted lithographic plates with desirable aluminum
10 substrates and their corresponding commercially-accepted development solutions can be used
11 without modification. A plate prepared by the present invention is functionally similar to a plate
12 prepared by photographic imaging, with a potential long run life but without the complexity, cost,
13 or waste of a film negative. The plate can be prepared quickly, in that fewer steps are required
14 and in that a speedy ink jet printer can be employed, and yet the plate image is of high resolution,
15 enabling high quality 4-color printing. Further, the plate thus prepared is storage stable, little
16 subject to contamination in its hydrophilic areas and can be used on a wide variety of
17 commercially available and accepted printing presses. The formulation of the insolubilizing fluid
18 is flexible and can be simple, inexpensive to manufacture, environmentally safe, and non-toxic.
19 Water can be used as a vehicle resulting in small drops that easily penetrate PS coatings
20 facilitating intimate mixing of the insolubilizing chemical with the reactive constituents of the
21 coating. The chemicals used in the fluid in this invention that enable insolubilization to occur on
22 negative and photo-exposed positive plates cover a wide range of materials. That such a simply

1 and flexibly formulated ink can be jetted in very small diameter drops to produce high resolution
2 images on conventional and widely accepted positive and negative working plates is a unique and
3 surprising result. That commercially available positive plates can be economically and
4 efficiently imaged by ink jet in a negative working process is a unique and surprising result.
5 Printers already using positive plates for printing requiring light imaging exposure can now use
6 efficient and economical ink jet negative imaging without having to switch plate types.

7 Still other objects and advantages will become apparent from the claims, and from a
8 consideration of the ensuing detailed description of the invention.

9 **BRIEF DESCRIPTION OF THE DRAWINGS**

10 FIG. 1 is a cross-sectional perspective view of a conventional developing processor in a preferred
11 configuration according to the prior art;
12 FIG. 2 is a block diagram flowchart depicting the process in which an on-press developable
13 printing plate is imaged by ink jet, developed on press, and then used in a printing operation;
14 FIG. 3 is a block diagram flowchart depicting a process in which an image reversal technique is
15 used to negatively image a presensitized printing plate by ink jet;
16 FIG. 4 is a continuation of the flowchart of Fig. 3; and
17 FIG. 5 shows the essential elements of a computer-to-press system comprising an ink jet
18 printhead enabling in situ imaging of a printing plate mounted on press.

19

1 DETAILED DESCRIPTION OF THE INVENTION

2 The invention comprises a subtractive process for preparing a printing plate for press by
3 imagewise applying an insolubilizing chemical to a coated plate, completing the insolubilization
4 reaction by heating if necessary, and washing the plate with a developing solution. The
5 insolubilizing chemical undergoes a chemical reaction with, or facilitates a chemical reaction in,
6 the plate coating, making the reacted coating insoluble to a developing solution in which the
7 unreacted coating is soluble. In the case of an on-press developable plate, the developing step is
8 effectively performed using the working fluids of the press, i.e., the press fountain solution and
9 ink.

10 A computer-to-plate system according to the invention preferably comprises an ink jet
11 printer (IJP) and a developing processor. To facilitate accurate imaging of the plate, the paper-
12 handling or substrate-handling subsystem of ink jet printer should have a short, straight paper
13 path. A printing plate is generally stiffer and heavier than the paper or media typically used in
14 commercially available ink jet printers. If the plate fed into the printer mechanism must bend
15 before or after being presented to the imaging print head, then the movement of the plate through
16 the printer may not be as accurate as the media for which the printer was designed. The most
17 preferred EPSON STYLUS COLOR 3000 has such a short, straight paper path. A platen is
18 preferably placed at the entrance to the paper feed mechanism. The platen preferably has a
19 registration guide rail and supports the plate as it is pulled into the printer by the feed
20 mechanism, facilitating the accurate transport of the plate under the imaging print head.

21 In the most preferred embodiment, the IJP used is a commercially available drop-on-
22 demand printer capable of printing small ink drops having volumes no larger than 8 picoliters

1 (8 pl) such as the EPSON STYLUS COLOR 3000 ink jet printer available from Epson America,
2 Inc., Long Beach, CA. However, the great flexibility available to the practitioner in formulating
3 an insolubilizing fluid according to the invention means that a well-performing jettable solution
4 can be formulated such that the print head of almost any ink jet printer will be able to form
5 regular drops with good reliability.

6 Because the powerful solvating capability of water, aqueous ink jet drops typically
7 penetrate the imaged media. Without being bound by theory, it is believed this may be important
8 to the invention because it is probably necessary for the insolubilizing chemical to be brought
9 into intimate contact with the reactive constituents of the plate coating to effect insolubilization.
10 Although water is the most preferred fluid vehicle, it is also possible to use other penetrating
11 solvents such as methyl ethyl ketone, ethyl acetate, ethyl lactate, dimethyl formamide, acetone,
12 simple alcohols, and other like chemicals or mixtures of such chemicals. Typically, the vehicle
13 would comprise 30 to 99 percent of the imaging fluid.

14 In one embodiment of the invention, the insolubilizing agent comprises pH-elevating
15 agents typically of low molecular weight such as sodium carbonate, sodium bicarbonate, lithium
16 carbonate, lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium
17 tetraboratedecahydrate, sodium pyrophosphatedecahydrate, sodium phosphate, sodium
18 metasilicate, or amines such as ethanolamine, diethanolamine, triethanolamine, ethylamine,
19 propylamine, butylamine, imidazolines, substituted imidazolines such as 1-hydroxyethyl-2-
20 cocylimidazoline, 1-hydroxyethyl-2-caprylimidazoline, 1-hydroxyethyl-2-oleylimidazoline, and
21 1-hydroxyethyl-2-tall oil imidazoline, tall-oil fatty acid-diethylenetriamine imidazoline,
22 imidazoles, substituted imidazoles, amino amides, polyamines, or mixtures of such chemicals.

1 The pH range of the imaging fluid is between 7.5 and 14, and more preferably from about 8.0 to
2 12.5.

3 In another embodiment of the invention, the insolubilizing agent comprises one or more
4 amine salts prepared by the reactions of amines including imidazolines with either acids or with
5 quaternarizing agents. Examples of such amine salts are ammonium acetate, acetates of ethyl
6 amine, propyl amine and triethanol amine and related salts, 1-hydroxyethyl-2-cocylimidonium
7 sulfate, 1-hydroxyethyl-2-cocylimidonium acetate, imidonium acetate, 1-hydroxyethyl-2-
8 caprylimidonium hydroxyacetate, 1-hydroxyethyl-2-oleylimidonium phosphate, isostearyl
9 ethyylimidonium ethosulfate, acetates of amino amides and related compounds. The
10 insolubilizing agent typically comprises from 0.05 to 7 percent of the fluid, but in specific
11 instances can comprise as much as 25% of the fluid.

12 For reliable jetting, and so that during idle periods the fluid does not dry out in the ink jet
13 nozzle causing it to clog, a humidifying co-solvent may be added to the insolubilizing fluid. The
14 co-solvent can be a polyhydric alcohol such as glycerin, ethoxylated glycerin, ethylene glycol,
15 diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, or trimethylol
16 propane, other high boiling point liquids such as pyrrolidone, methylpyrrolidone, or triethanol
17 amine, other simple alcohols such as isopropyl alcohol or tertiary butyl alcohol, or mixtures of
18 such solvents. When used, the co-solvent would typically comprise 5 to 70 percent of the fluid.

19 A dye compatible with the insolubilizing agent can be added to the fluid at a level of a
20 few percent to enhance the visibility of the latent image. The insolubilizing fluid may contain
21 one or more surfactants or wetting agents to control the surface tension of the ink, enhancing
22 jettability, and to control the spread and penetration of the drop on the coated plate. The

1 surfactants and wetting agents may include acetylenic glycols, such as SURFYNOL 104,
2 SURFYNOL 465, SURFYNOL FS-80, SURFYNOL PSA-216, DYNOL 604, polyethoxylated
3 octyl phenols, such as TRITON X-100, and similar chemicals or mixtures of similar chemicals.
4 When used, surfactants and wetting agents typically comprise 0.001 to 10 percent of the fluid.

5 The insolubilizing fluid may also contain one or more biocides to prolong the shelf life of
6 the fluid. Suitable biocides include for example PROXEL GXL, solution of 1,2-benzothiazoline-
7 3-one, sodium hydroxide and dipropylene glycol, sodium OMADINE, 2-pyridinethiol-1-oxide,
8 sodium salt, DOWICIL, cis-1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride,
9 GIVGUARD DXN, and similar chemicals or mixtures of such chemicals. When used, the
10 biocide would typically comprise 0.1 to 3 percent of the ink. If the pH of the insolubilizing fluid
11 is over 10, it is not necessary to use a biocide and this is preferred.

12 A typical formulation for an insolubilizing fluid comprises:

13	Water with sufficient amount of insolubilizing agent	70%
14	Co-solvent	26%
15	Dye	3%
16	Surfactant	1%

17 Imagewise application of the insolubilizing fluid onto the plate coating using an ink jet
18 printhead results in a latent image on the plate. To complete preparation for use, it is then
19 necessary to develop the imaged plate. In one embodiment of the invention, it is preferable to
20 use a conventional developing processor. A most preferred processor configuration is illustrated
21 in Fig 1. An imaged plate is conveyed first through a hot air drying section 10, second through a
22 pre-heat oven 12, third through a development station 14 where the appropriate developing

1 solution is poured on the plate and the solubilized coating removed. Fourth, the plate is
2 conveyed through a rinse section 16, and finally, fifth through a post bake oven 18. The plate is
3 then ready to be used on press.

4 In another embodiment of the invention, illustrated in Fig. 2, an on-press developable plate is
5 imaged. In this embodiment, after imaging of the subtractive plate 20 by an ink jet printer 22, no
6 conventional development of the latent image 26 is required. Instead, the plate is first heated in
7 an oven 24 to dry the image and, without being bound by theory, complete the insolubilization
8 reaction. Second, the plate is mounted on the plate cylinder of a conventional offset lithographic
9 press 28. Third, the latent image is developed by operating the press such that the plate cylinder
10 is rotated and the working fluids of the press, i.e., the press ink and fountain solution, are applied
11 to the plate coating. The plate is then ready to be used to print images on paper or other media 30
12 by the normal operation of the press.

13

14 Positive Plate

15 In this aspect of the invention, as illustrated in Figs. 3 and 4, a method for preparing a
16 positive plate for press by an image reversal process comprises the steps of:

17 a) providing a conventional subtractive positive plate. A side view is shown 40.
18 b) Blanket exposing the plate coating using a light source 42. A side view of the
19 exposed plate is shown 44. A top view of the exposed plate is shown 46.
20 c) Applying imagewise an insolubilizing chemical to the coating preferably using
21 an ink jet printer 48;
22 d) heating the plate in an oven 50. The latent image on the plate is indicated 52.

1 e) Developing the plate in a conventional processor 54. The plate is then ready
2 for use 56.

3 The positive plate can be blanket light exposed just before the plate is chemically imaged.
4 The IJP can also be expanded to include a light exposure attachment placed on the printer before
5 the imaging printhead. In this expanded system, the blanket light exposure and chemical imaging
6 steps can be performed in a continuous operation. The plate can also be blanket light exposed at
7 the time of manufacture by including a light exposure step after drying and before packaging.
8 The latter procedure would eliminate a processing step for the user. Preferred light sources that
9 can be used in the blanket light exposure step are those that emit light in the wavelength range of
10 from about 290 to 500 nm. Suitable light sources are carbon arcs, mercury lamps, fluorescent
11 lamps and metal halide lamps.

12 After blanket exposure, a latent image is created in the coating of the plate by imagewise
13 application of a chemical that causes the affected area of the coating to become insoluble in the
14 developing solution. It is simplest and preferred to formulate a fluid solution comprising the
15 insolubilizing chemical, and to use an ink jet printer for the imagewise application of the
16 insolubilizing solution. As described above, effective insolubilizing agents can be bases
17 including amines, and amine salts.

18 According to this invention, without being bound by theory, when the positive plate is
19 first given a blanket light exposure the o-quinone diazide compound is converted into a
20 carboxylic acid that renders the coating soluble in dilute aqueous alkaline solutions. An
21 insolubilizing fluid is then imagewise jetted onto the light exposed plate followed by a brief heat
22 treatment of the plate. During the heat treatment step, decarboxylation is believed to occur only

1 in the areas on the plate that were jetted with fluid. In these decarboxylated areas, the coating is
2 no longer soluble in dilute aqueous alkaline solutions such as typical positive plate developing
3 solutions. When treated with such dilute alkaline solutions in the development step, all the
4 coating is removed from the plate except in the areas where the fluid has been jetted. A reverse
5 image is thus produced. The plate is then ready to be mounted and used in a conventional press.

6 Note that this process, termed an “image reversal” process as used herein is somewhat
7 different than the typical light-based image reversal processes used in photolithographic
8 applications in that it is usually necessary to follow the imagewise application of the chemical by
9 a heating step. Further, the imaging step is carried out after the blanket exposure step rather than
10 before because the carboxylic acids in the coating need to be created via the blanket exposure
11 step before they can be decarboxylated in the imaging and heating steps. In a prior art
12 application of image reversal for the purpose of imaging printing plates described in
13 US 4,927,741, the blanket exposure step follows the heat treatment, which reduces the
14 effectiveness of the blanket exposure step in solubilizing the non imaged areas of the coating. In
15 this patent, a cumbersome method to minimize this problem is described which requires that the
16 blanket exposure step be carried out while the coating is submerged under water.

17 The concentration of the active ingredient, the decarboxylating agent, in the insolubilizing
18 fluid can range from about 0.05 to 20 percent or preferably from about 0.1 to 3.5 percent. A dye
19 compatible with either the alkaline materials or the amine salts can be added to the fluid at a level
20 of a few percent to enhance the visibility of the latent image.

21 After application of the insolubilizing chemical, the plate is heated for the purpose of
22 completing the insolubilization reaction. The extent of the heat treatment required is dependent

1 on the particular o-quinone diazide that is incorporated in the coating. A coating made from an
2 o-quinone diazide having the sulfonic acid ester group in the same ring as the quinone diazide
3 group requires a less vigorous heat treatment than one where the two groups aren't in the same
4 ring. If the plate coating is made from an o-naphthoquinone -1,2-(diazide-2)-5-sulfonic acid
5 ester, it is preferably heated to between 55 to 130°C for from 15 seconds to 10 minutes or most
6 preferably from about 90 to 110°C for 1 to 2 minutes. If the plate coating is made from an o-
7 naphthoquinone-1,2-(diazide-2)-4-sulfonic acid ester, it is preferably heated to between 40 to
8 110°C for from 3 seconds to 5 minutes or most preferably from about 50 to 60°C for from 30 to
9 90 seconds. The maximum heat treatment that can be applied is limited by the heat treatment
10 conditions of time and temperature that would cause decarboxylation to occur in the non-
11 chemically imaged areas of the coating. After heating, the plate is developed either by hand or
12 preferably with a conventional developing processor using a conventional developing solution to
13 produce the image.

14 As described above, the insolubilizing fluid applied to the light exposed positive plate is
15 believed to react by decarboxylating the carboxylic acid that forms from the o-quinone diazide
16 during photo-exposure. The elimination of the carboxylic group in one of the chemicals in the
17 lithographic plate coating changes its alkaline solubility from soluble to insoluble. When the
18 plate is processed by the developing solution, a dilute aqueous alkaline solution, the unprinted
19 areas of the coating are quantitatively dissolved, leaving the hydrophilic-treated aluminum bare,
20 and the printed areas coating are apparently undisturbed.

21 The concentration of the o-quinone diazide in the positive plate can vary over wide limits.
22 In general, the proportion is 5 to 50 percent and more preferably between 20 and 40 percent,

1 based upon weight. The concentration of the resin component is from about 50 to 95 percent and
2 more preferably from 60 to 80 percent. The resin component can be used without any addition of
3 a separate o-quinone diazide compound if the resin has o-quinone diazide groups covalently
4 bonded to it. The coating thickness of the positive coating can range from about 0.4 to 4
5 grams/square meter. The preferred o-quinone diazides are naphthoquinone-1,2-(diazide-2)-5-
6 sulfonic acid esters and naphthoquinone -1,2-(diazide-2)-4-sulfonic acid esters. They are
7 prepared by the reactions of the corresponding sulfonyl chlorides with alcohols and phenols. The
8 preferred phenolic compounds for these reactions are cresol-formaldehyde resins, di, tri, tetra,
9 and poly hydroxy aromatics either unsubstituted or substituted with other groups. Some examples
10 of such phenolic compounds are resorcinol, phloroglucinol, 2,3,4-trihydroxybenzophenone and
11 tetrahydroxybenzophenone.

12 The developer used for this invention is similar to the typical dilute aqueous alkaline
13 solutions used on positive plates. They preferably have a pH of 11 or higher. Illustrative of the
14 various bases that can be used to adjust the alkalinity of the developer are sodium hydroxide,
15 potassium hydroxide, sodium silicate, potassium silicate, sodium metasilicate, potassium
16 metasilicate, sodium phosphate, sodium dihydrogen phosphate, ethanolamine or mixtures of such
17 chemicals. Surfactants are also added to the developer and include such anionic surfactants as
18 sodium alkylbenzenesulfonates, sodium alkynaphthalenesulfonates and sodium
19 dialkylsulfosuccinates at concentrations from about 0.003 to 3 percent by weight.

20 In this invention, the use of positive plates together with their respective developers is
21 highly desirable and advantageous. Positive plates have outstanding stability; some such plates
22 have a shelf-life of more than two years when stored at room temperature. They also have

1 excellent resolution and produce images that have a long press-life that is greatly extended by a
2 bake process when heated at about 250 to 280°C for about 1 to 3 minutes. The image reversal
3 process doesn't detract from these properties. The developers used on the positive plates are
4 ecologically acceptable; they don't contain any undesirable volatile organic chemicals.

5 The following non-limiting examples serve to illustrate the invention.

6

7 EXAMPLE 1

8 Prepare a solution of 29.6 grams ALNOVOL PN-430, a cresol formaldehyde novolac
9 resin available from Hoechst in 308 grams ethyl lactate. To 50 grams of this solution, add 2.7
10 grams of POSITIVE DIAZO LL, a naphthoquinone-1,2-(diazide-2)-5-sulfonic acid ester
11 available from Molecular Rearrangement Inc. of Newton, NJ (MRI) which is made by the
12 reaction of naphthoquinone-1,2-(diazide-2)-5-sulfonyl chloride with 2,2'-thiobisnaphthol. In this
13 reaction, mono and sulfonic acid esters can form. The molar ratio of the two reactants in the
14 manufacture of POSITIVE DIAZO LL is adjusted so that the product that is produced is a
15 mixture of 60% disulfonic acid ester and 40% monosulfonic acid ester. The solution is coated
16 onto a grained, anodized and silicated aluminum sheet using a number 10 wire wound rod
17 followed by drying with a hot air dryer. The entire plate is blanket exposed to 20 units of light
18 using the high intensity setting of a MAGNUM PLATEMAKER. Microdrops of 1% aqueous
19 solutions of sodium metasilicatepentahydrate and sodium carbonate together with a 1% solution
20 of triethanolamine in a solvent mixture of 25 parts acetone and 75 parts water are then applied.
21 The treated coating is then heated for 10 minutes at 110°C followed by development with an
22 alkaline solution of the following composition:

SUBSTITUTE SPECIFICATION

1	Sodium metasilicatepentahydrate	55 grams
2	(from the PQ Corp. under the name PENTABEAD 20)	
3	AEROSOL OS Surfactant from Cytec	2.2 grams
4	Water	1000 ml
5	The parts of the coating where the drops are applied are insolubilized in the developer by the heat	
6	treatment. The other parts of the coating are still soluble in the developer after the heat	
7	treatment. During development, they are quantitatively removed leaving the hydrophilically treated	
8	aluminum bare. Images are produced on the coated plate from the sodium carbonate and sodium	
9	metasilicate solutions that correspond to the size of the drops of the applied solutions. Spreading	
10	of the triethanolamine solution occurs when it is applied onto the coating. It produces a larger	
11	image than the original size of the drops. The spreading of the drop is attributed to the presence	
12	of acetone in the solution.	

13 The above-coated plate is a positive plate. When light exposed and developed in the usual
14 manner without any chemical treatment, a positive image is produced.

15

1 EXAMPLE 2

2 In this example, a positive plate, commercially available from LASTRA (FUTORO-
3 ORO) of Sulmona, Italy is evaluated. It is comprised of an o-naphthoquinone diazide -5-sulfonic
4 acid ester and alkali soluble resins together with dyes and indicator dyes. The LASTRA plate is
5 blanket light exposed by the procedure used on the coating from Example 1. Drops of 1%
6 sodium carbonate are applied onto the exposed plate followed by heating at 120°C for 4 minutes.
7 After development by the alkaline developer solution used in Example 1, an excellent image is
8 produced that corresponds to the size of the applied drops. During the heat treatment, the coating
9 is only insolubilized where the sodium carbonate solution is applied.

10

11 EXAMPLE 3

12 This example describes image formation on the LASTRA positive plate using
13 MONAZOLINE C, 1-hydroxyethyl-2-cocoylimidazoline available from Uniqema in New Castle,
14 DE.

15 Prepare the following solutions:

		A	B	C	D
17	MONAZOLINE C	0.25g	0.25g	0.18g	0.09g
18	Isopropyl Alcohol	2.5g	7.5g	5.5g	4.5g
19	Glycerine	--	--	2.0g	4.5g
20	Water	8g	62.5g	22.5g	45g

1 A LASTRA positive plate is blanket light exposed by the procedure used on the coating from
2 Example 1. Drops of the solutions A through D are applied onto the coating. Parts of the
3 coating where solution:
4 1. A is applied are heated at 120°C for 1 minute,
5 2. B is applied are heated at 105°C for 45 seconds and also at 95°C for 1 minute,
6 3. C is applied are heated at 95°C for 1 minute and
7 4. D is applied are heated at 95°C for 30 seconds and also at 70°C for 1 minute.
8 After development by the alkaline developer described in Example 1, excellent images are
9 produced by the four solutions on all the plates that are differently heat treated. When the
10 imaged plates are treated with water and then rubbed with a WEBRIL wipe that is saturated with
11 water and a lithographic ink, the images are inked while the aluminum in the non-imaged areas
12 don't absorb any ink. This example illustrates that image formation takes place from solutions of
13 MONAZOLINE C over a wide concentration range and that the time and temperature of the
14 heating step are also over a wide range.

15

16 EXAMPLE 4

17 This example illustrates image formation using MONAZOLINE C ACETATE, which is
18 prepared by the addition of acetic acid to an aqueous dispersion of MONAZOLINE C. Prepare
19 the following solutions:

	A	B	C
21 MONAZOLINE C	0.3	0.3g	0.3g
22 Water	60ml	60ml	60ml

1 Acetic Acid, 3.4% 1.0g 1.7g 2.1g

2 The pH of Solutions A, B and C is 10, 7 and 5, respectively. The pH of the
3 MONAZOLINE C solution without the addition of acetic acid is 11. MONAZOLINE C
4 ACETATE is water soluble and upon the addition of acetic acid, MONAZOLINE C is
5 solubilized. The LASTRA positive plate is blanket light exposed by the procedure described in
6 Example 1. Drops of the three solutions are applied onto the plate and then heated at 100°C for 1
7 minute. After development with the alkaline developer, excellent images are produced where the
8 drops are applied that correspond to the size of the applied drop. The images were unaffected by
9 rubbing vigorously with a WEBRIL wipe that is wet with the alkaline developer and is indicative
10 of its excellent adhesion and chemical resistance. The low pH of Solution C is an indication that
11 in addition to the formation of the acetate salt of the imidazoline, some unreacted acetic acid is
12 present which doesn't detract from its decarboxylating properties.

13

14 EXAMPLE 5

15 This example illustrates image formation on the LASTRA positive plate using
16 triethanolamine. Prepare a solution of:

17 Triethanolamine 0.3g

18 Isopropyl Alcohol 3g

19 Water 62g

20 Apply the solution onto the blanket light exposed plate and after heating at 110°C for
21 2 minutes followed by development in the usual manner, satisfactory images are produced where
22 the drops are applied.

1

2 EXAMPLE 6

3 This example illustrates image formation using imidazole. Prepare a solution of:

4 Imidazole from BASF 3g

5 Ethanol 10g

6 Water 90g

7 Apply the solution onto a blanket light exposed LASTRA plate and then heated at 90°C

8 for 90 seconds followed by alkaline development. Satisfactory images are produced where the

9 solution is applied. The pH is 8.5 for the 1% imidazole solution.

10

11 EXAMPLE 7

12 This example illustrates image formation with MONAZOLINE O and T and the

13 evaluation of three other commercially available positive plates based on naphthoquinone-1,2-

14 (diazide-2))-5-sulfonic acid esters, CAPRICORN DH from KPG in Norwalk, CT;

15 STEINBACHER ELAN SP 123 from Steinbacher Polymer GMBH in Germany and the INKKER

16 positive plate from Inkker Systems Corp. in Seoul, Korea. Prepare solutions:

		A	B	C
17				
18	MONAZOLINE T, Tall Oil Hydroxyethyl Imidazoline,	0.2g	--	--
19	from Uniqema			
20	MONAZOLINE O, Oleyl Hydroxyethyl Imidazoline,	--	0.2g	--
21	from Uniqema			
22	MONAZOLINE C	--	--	0.4g

1	Ethyl Lactate	4g	3g	--
2	Glycerin	2g	2g	--
3	Water	25g	25g	25g
4	Acetic Acid, 3.4%	--	--	1.5g

5 All three plates are blanket light exposed to 20 units of light from the high intensity
6 setting of the MAGNUM PLATEMAKER. Drops of solutions A and B are applied onto the
7 KPG and STEINBACHER plates which are then heated at 105°C for 1 minute followed by
8 development with the dilute aqueous alkaline solution used in Example 1. On both plates the
9 only areas where the coating was insoluble and remained on the plate was where the drops were
10 applied. Excellent images are produced that correspond to the size of the applied drops. The
11 unexposed coating is completely removed leaving the aluminum hydrophilic in those areas.

12 Drops of solution C are applied onto the INKKER plate that is then heated at 105°C
13 followed by development as previously described in this example. Excellent images are produced
14 where the drops are applied and in the other areas the coating is completely removed leaving the
15 aluminum hydrophilic.

16

17 EXAMPLE 8

18 This example illustrates image reversal of positive plates using isostearyl ethylimidonium
19 ethosulfate available from Uniqema Corp.under the name MONOQUAT ISIES and evaluates a
20 positive plate made with the same ingredients as the one described in example 1 except that it
21 contains two additional ingredients, a dye and an indicator dye. Prepare a solution of:

22 Ethyl Lactate 44g

1 Diazo LL 2.69g
2 ALNOVOL PN-430 4.32g
3 Victoria Blue Dye 0.07g
4 Sudan M Yellow 150 from BASF 0.07g

5 which is coated onto a grained, anodized and silicated sheet of aluminum using a number 10 wire
6 wound rod and dried with a hot air blower. Prepare solutions of:

	A	B
8 MONOQUAT ISIES	0.40G	--
9 MONAZOLINE C	--	0.25g
10 Isopropyl Alcohol, 70%	4g	--
11 Ethyl Lactate	--	3g
12 Glycerin	0.75g	2g
13 Water	25g	25g

14 The pH of Solution A is 6.5. After blanket light exposure of the positive plate, apply drops of
15 solutions A and B and then heat for 1 minute at 105°C . The coating is insolubilized where the
16 drops are applied. After development by the alkaline developer, excellent images are produced
17 and the aluminum in the non-imaged areas is hydrophilic. Drops of solution A are also applied
18 to a blanket light exposed positive plate of Inkker Systems Corp. which after heating at 105°C
19 for 1 minute followed by development with the alkaline developer produce excellent images. The
20 only areas of the coating that are insoluble in the developer are where the drops are applied.

21

22 EXAMPLE 9

1 This example illustrates image formation using an amino amide and its corresponding
2 acetate that are produced from MONAZOLINE C, coycoyl hydroxyethyl imidazoline. In the
3 presence of water MONAZOLINE C and its acetate salt will gradually hydrolyze to produce an
4 amino amide and an acetate salt, respectively. Prepare solutions of:

	A	B
6 MONAZOLINE C	0.2g	0.25g
7 Ethyl lactate	--	3g
8 Glycerine	--	0.75g
9 Water	40g	25g
10 Acetic Acid, 3.4%	1.4g	--

11 The two solutions are stored at room temperature for two months and within this period
12 hydrolysis is believed to occur to produce the amino amide and amino amide acetate. Drops of
13 the two solutions are applied onto the blanket light exposed positive plates of the one prepared in
14 Example 8 and of the Inkker Systems Corp. They are then heated at 105°C for 1 minute
15 followed by development with the alkaline developer. Excellent images are produced where the
16 drops are applied and in the other areas the coating is readily removed.

17

18 EXAMPLE 10

19 This example illustrates image reversal of positive plates using the sulfate and phosphate
20 salts of MONAZOLINE C and using WITCAMINE TI-60, tall-oil fatty acid-diethylenetriamine
21 imidazoline, ethoxylated available from the Crompton Corporation. The LASTRA positive plate
22 is blanket light exposed as previously described. Prepare solutions of:

	A	B	C	D	E
2	MONAZOLINE C	0.23g	0.23g	0.23g	0.23g
3	WITCAMINE TI-60	--	--	--	--
4	Water	40ml	40ml	40ml	40ml
5	Sulfuric Acid, 3.4%	1g	1.4g	--	--
6	Phosphoric Acid, 3.4%	--	--	1g	1.6g
7	pH	8	4	8.5	4
8	Drops of the five solutions are applied onto the blanket exposed LASTRA plate, which is then				
9	heated at 110°C for 2 minutes followed by development by the dilute aqueous alkaline developer.				
10	The coating is only insoluble in the developer where the drops are applied. On development,				
11	excellent images are produced. A 3.4% aqueous solution of phosphoric acid containing 10%				
12	ethanol when applied onto the blanket light exposed LASTRA plate followed by heating at				
13	110°C for 3.5 minutes didn't insolubilize the coating in the dilute aqueous developer. This				
14	indicates that the phosphoric acid that is present in Solution D is not insolubilizing the LASTRA				
15	plate.				

16

17 EXAMPLE 11

18 This example illustrates image reversal using N-acetylenediamine and its acetate
19 salt. Prepare solutions of:

	A	B	
2	N-acetylenediamine	0.22g	0.22g
3	Glycerine	1g	1g
4	Isopropyl alcohol, 70%	4g	4g
5	Ethyleneglycol monobutyl ether	0.22g	0.22g
6	Glycerine	1g	1g
7	Isopropyl alcohol, 70%	4g	4g
8	Ethyleneglycol monobutyl ether	0.4g	--
9	Acetic acid, 3.4%	--	2.6g
10	The pH of Solutions A and B are 10.5 and 8.5, respectively. After blanket light exposure of the		
11	LASTRA positive plate, apply drops of the two solutions followed by heating the plate at 110°C		
12	for 4 minutes. Excellent images are formed on development where the drops are applied. The		
13	non- chemically treated parts of the coating are readily dissolved in the alkaline developer.		

14

15 EXAMPLE 12

16 This example illustrates the use of a positive plate in the image reversal process that is
17 made with an o-naphthoquinone-1,2-(diazide-2)-4-sulfonic acid ester. Prepare a solution of:

18	ALNOVOL PN-430	4.32g
19	2,1,4 Diazo Ester D-42 from MRI, CAS# 80296-78-2	2.69g
20	Ethyl Lactate	44g
21	Victoria Blue Dye	0.085g
22	Sudan M Yellow 150	0.070g

1 The solution is coated onto a grained, anodized and silicated aluminum sheet using a number 10
2 wire wound rod followed by drying with a hot air dryer. Drops of the phosphate salt of
3 MONAZOLINE C which is Solution B of Example 10 is applied onto this plate that is blanket
4 light exposed in the previously described manner followed by heating at 60°C for both 15 and 30
5 seconds. Where the drops are applied, the coating is insoluble while the non-chemically treated
6 coating is soluble in the dilute aqueous alkaline developer solution prepared in Example 1. On
7 development, an image forms where the drops are applied and the coating is quantitatively
8 removed in the unimaged areas leaving the hydrophilically treated aluminum bare. This example
9 is the only one that uses a naphthoquinone-1,2-(diazide-2)-4-sulfonic acid ester instead of -5-
10 sulfonic acid esters. Such coatings decarboxylate at lower temperatures both when chemically
11 and non-chemically treated. For example, when the coating prepared in this example is heated at
12 80°C for only 30 seconds, it is insolubilized in the developer.

13

14 **On-Press Developable Plate**

15 In another aspect of the invention, the method for preparing an on-press developable plate
16 for printing comprises the steps of:

- 17 a) providing an on-press developable plate;
- 18 b) applying imagewise an insolubilizing chemical to the plate coating;
- 19 c) heating the plate;
- 20 d) mounting the plate on the plate cylinder of a conventional offset lithographic press;
- 21 e) operating the press such that the press working fluids are applied to the plate coating.

1 A variety of photopolymer chemistries can be used to create on-press developable
2 coatings for lithographic plates. Often such plate coatings comprise acrylate monomers such as
3 benzyl acrylate, benzyl methacrylate, butoxyethyl acrylate, butoxymethyl methacrylate,
4 cyclohexyl acrylate, cyclohexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl
5 methacrylate, glycidyl acrylate, glycidyl methacrylate, methyl methacrylate, ethyl methacrylate,
6 butyl methacrylate, phenoxyethyl acrylate, phenoxyethyl methacrylate, phenyl methacrylate,
7 ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, diethyleneglycol diacrylate,
8 diethyleneglycol dimethacrylate, triethyleneglycol diacrylate, triethyleneglycol dimethacrylate,
9 tetraethyleneglycol diacrylate, tetraethyleneglycol dimethacrylate, polyethyleneglycol diacrylate,
10 polyethyleneglycol dimethacrylate, neopentylglycol diacrylate, neopentylglycol dimethacrylate,
11 ethyleneglycolbisglycidyl diacrylate, ethyleneglycolbisglycidyl dimethacrylate,
12 trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, glycerol diacrylate, glycerol
13 dimethacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, and pentaerythritol
14 tetramethacrylate. Such plate coatings typically also comprise photoinitiators such as 2,2-
15 dimethoxy-2-phenylacetophenone, benzophenone, benzil and its ketals, ketocoumarin, xanthone,
16 anthraquinones, tris[4-(dimethylamino)phenyl]methane, benzoin, 4,41-
17 bismethoxymethyldiphenylether, and benzoin ethers.

18 Such plate coatings are well known in the art and are described in U.S. Pat.
19 Nos. 5,514,522; 5,516,620; 5,556,924; 5,599,650; 5,607,816; 5,677,108; 5,677,110; 5,795,698;
20 5,811,220; 5,997,993; 5,620,822; 5,910,395; 5,925,497; 5,849,462; and 6,027,857 incorporated
21 herein by reference. Commercially available on-press developable plates include the KEMFRE
22 from Spectratech of Wake Forest, North Carolina, and the most preferred DIRECTPRINT from

1 KPG of Norwalk, Connecticut. The DIRECTPRINT plate coating comprises acrylate monomers
2 such as pentaerythritol triacrylate and free radical photoinitiators such as 2-
3 isopropylthioxanthone (QUANTACURE available from Biddle Sawyer, New York) and tris[4-
4 (dimethylamino)phenyl]methane (Crystal Violet leucobase). The DIRECTPRINT plate coating
5 does not contain substantial carboxylic acid functionality such that an esterification reaction
6 could result in image-worthy insolubilization.

7 In the invention described hereinabove the plate coatings comprise photosensitive free
8 radical initiators so that the insolubilization reaction can be initiated by light exposure. In
9 another aspect of the invention, a proprietary polymer plate coating can comprise acrylate
10 monomers and free radical initiators as described hereinabove. However, it may be desired to
11 manufacture a proprietary plate coating optimized for the process of imaging by chemical
12 insolubilization. In such a proprietary coating, it would be advantageous to use nonphotosensitive
13 free radical initiators such as organic or inorganic peroxides or azos so that the user need not be
14 concerned about incidental light exposure. Suitable peroxide initiators include dicumyl peroxide,
15 2,5-dimethyl-2,5-di(tbutylperoxy)hexane, di-t-butyl peroxide, t-butylperoxy benzoate, 2,5-
16 dimethyl-2,5-di(t-butylperoxy)hexane-3 and lauryl peroxide. Suitable azo free radical initiator
17 compounds include azoisobutyronitrile and dimethylazoisobutyronitrile, and azo-bis-4-cyano-
18 pentoic acid.

19 As an alternative to using nonphotosensitive free radical initiators, photoinitiators that
20 require co-synergists can be used to produce nonphotosensitive coatings by incorporating only
21 the photoinitiator together with acrylic monomers in a coating. The coating then can be
22 chemically imaged by the imagewise application of a co-synergist that would initiate the

1 polymerization reaction in a subsequent heat treatment step. Illustrative of some such systems
2 are: a 2,4,5-triphenylimidazoyl dimer consisting of two lophine radicals bound together by a
3 single covalent bond as the photoinitiator, and a free radical producing hydrogen donor or an
4 active methylene compound and a p-aminophenyl ketone as co-synergists as described in U.S.
5 Pat. Nos. 3,479,185 and 3,615,567 respectively, incorporated herein by reference, and the use of
6 tertiary amines as co-synergists with thioxanthone photoinitiators as reported in Eur. Polym. J.
7 No. 10, 841 (1985) incorporated herein by reference.

8 For photopolymer plates including on-press developable plates such as described above,
9 the insolubilizing agent comprises pH-elevating agents typically of low molecular weight such as
10 sodium carbonate, sodium bicarbonate, lithium carbonate, lithium hydroxide, sodium hydroxide,
11 potassium hydroxide, sodium tetraboratedecahydrate, sodium pyrophosphatedecahydrate, sodium
12 phosphate, sodium metasilicate, or amines such as ethanolamine, diethanolamine,
13 triethanolamine, ethylamine, propylamine, butylamine, imidazolines, substituted imidazolines
14 such as 1-hydroxyethyl-2-cocylimidazoline, 1-hydroxyethyl-2-caprylimidazoline, 1-hydroxyethyl-
15 2-oleylimidazoline, and 1-hydroxyethyl-2-tall oil imidazoline, tall-oil fatty acid-
16 diethylenetriamine imidazoline, imidazoles, substituted imidazoles, amino amides, aromatic
17 amides, polyamines, or mixtures of such chemicals. The insolubilizing agent typically comprises
18 from 0.1 to about 7.5 percent of the fluid. The pH range of the imaging fluid is between 7.5 and
19 13.5, and more preferably from about 8.0 to 12.5.

20 A most preferred insolubilizing fluid consists of 1% poly(ethylenimine) (Mw = 25,000;
21 Mn = 10,000) available from Aldrich, 98.9% water, and 0.1% of the surfactant FS-80 available
22 from Air Products. After imagewise application of the insolubilizing fluid by IJP, it is most

1 preferred to convectively heat the plate for about 60s at about 120C, taking care not to
2 excessively expose the plate to ambient light. The plate is then ready to be mounted on press,
3 developed according to standard procedure, and used for printing.

4 Because of their high aqueous solubility and their effectiveness at low concentrations, it is
5 possible to formulate insolubilizing fluids with polyethylenimines that are both long-term shelf
6 stable and long-term compatible with ink jet printhead materials and components. Without being
7 bound by theory, it is believed that primary and secondary amines such as the polyethylenimines
8 act as a co-synergists in conjunction with the 2-isopropylthioxanthone photoinitiator of the
9 DIRECTPRINT plate to reduce the thermal stability of the coating in the imaged areas. Thus
10 crosslinking of the plate coating occurs exclusively in the imaged areas during the convective
11 heating step.

12 The following non-limiting examples serve to further illustrate the invention.

13

14 EXAMPLE 13

15 A marking fluid was mixed with the following components: 98.90 g of distilled water,
16 1.00 g of poly(ethylenimine) (Mw = 25,000; Mn = 10,000), and 0.10 g of FS-80 surfactant (Air
17 Products and Chemicals). This solution was injected into an ink cartridge and charged into an
18 Epson 3000 printer. An image was jetted onto a KPG DIRECTPRINT plate, which was then
19 baked in an oven at 230°F for 3 minutes. The plate was mounted on a rotary offset press,
20 developed according to the manufacturer's instructions and used to print black ink on standard
21 copier paper stock. 900 images were printed with no evidence of plate wear. The image was
22 clean, the lines clear, and the individual image dots were undamaged. Dot diameters on the plate

1 averaged ~ 54 µm. Dot diameters on paper averaged ~ 80 µm. Alternatively, a DIRECTPRINT
2 plate so imaged was passed through a convection conveyor oven set at 260°F for an exposure
3 time of 90 seconds. Press results were similar.

4 That hundreds of impressions with good image quality can be obtained from a chemically
5 insolubilized negative working PS plate without a baking step after development is a unique and
6 surprising result.

7

8 EXAMPLE 14

9
10 A marking fluid analogous to that described in Example 13 was mixed, except that the
11 polyethylenimine had a number average molecular weight (Mn) of 600. A KPG DIRECTPRINT
12 plate was processed in the exact same way as in Example 13. This also yielded durable images
13 when developed on press with black ink; no wear was observed after 100 impressions. The dots
14 on both the plate and the paper were about 25% larger than those in Example 1, and the resulting
15 images were thus much darker.

16

17 EXAMPLE 15

18 A marking fluid was prepared as in Example 13, except that the polyethylenimine had an
19 Mn = 423. The plate was imaged with this fluid and then heated in the exact same way as in
20 Example 13. This also yielded durable images when developed on press with black ink. No
21 wear was observed after 100 impressions. The dots on both the plate and the paper were about
22 25% larger than those in Example 13, and the resulting images were thus much darker. It is
23 believed that the high average molecular weight of the polyethyleneimine polymer in Example 13

1 inhibits the insolubilizing agent from spreading through the coating during the heating step and
2 thus facilitates the desired small dot size.

3

4 EXAMPLE 16

5 A marking fluid was mixed with the following components: 98.90 g distilled water, 1.00 g
6 pentaethylenehexamine, and 0.10 g FS-80 surfactant. A KPG DIRECTPRINT plate was imaged
7 with this fluid and heated similar to Example 13. This yielded good images when developed on
8 press with black ink. The dot size on the paper was ~ 100 µm.

9

10 EXAMPLE 17

11 A marking fluid was mixed with the following components: 69.50 g distilled water, 5.00
12 g glycerine, 25.00 g diethylene glycol, and 0.50 g pentaethylene hexamine. This solution was
13 injected into an ink cartridge and charged into an EPSON 3000 printer. An image was jetted onto
14 a KPG DIRECTPRINT plate, which was then baked at 230°F for three minutes. The plate was
15 transferred to a rotary offset press, developed according to the manufacturer's directions, and
16 used to print black ink on standard copy paper stock. 100 prints were produced with little or no
17 sign of degraded image wear. This was typical performance of marking fluids employing the
18 lower molecular weight oligomers of ethylenimine.

19

20 EXAMPLE 18

21 Marking fluids were mixed with the following components: 20.00 g distilled water, 1.00 g of
22 ANCAMIDE 50X (X = 0, 1, 2, 3, or 7) which are available from Air Products, 2.40 g ethyl

1 lactate, and 0.55 g glycerine. Each of these fluids was pipetted down in small drops on separate
2 areas of a KPG DIRECTPRINT plate, which was then baked at 230°F for 15 minutes. This plate
3 was transferred to a rotary offset press and used to print black ink on standard copy paper stock.
4 1000 prints could be generated with little or no sign of degradation or wear of the dots for each of
5 the ANCAMIDE chemicals tested.

6

7 EXAMPLE 19

8 A marking fluid was mixed with the following components: 100.00 g distilled water,
9 5.00 g of ANCAMIDE 500 (Air Products and Chemicals), 12.00 g ethyl lactate, and 2.75 g
10 glycerine. This solution was used analogously to Example 16 in producing an image on a KPG
11 DIRECTPRINT plate, which was then baked at 230°F. for 15 minutes, then transferred to a
12 rotary offset press, developed, and used to print black ink on standard copy paper stock. 100 to
13 300 prints could be produced with little or no sign of degraded image wear. Large dots
14 (> 100µm) were printed on the paper. This experiment was repeated with ANCAMIDES 501,
15 502, 503, and 507; all resulted in similarly durable images.

16

17 EXAMPLE 20

18 A marking fluid was mixed with the following components: 100.00 g distilled water,
19 1.00 g MONAZOLINE C (from Uniqema), 12.00 g ethyl lactate, and 2.75 g glycerine. Similar
20 fluids were also mixed with MONAZOLINE O, and MONAZOLINE T in place of the
21 MONAZOLINE C. Each of these fluids was pipetted down in small drops on separate areas of a
22 KPG DIRECTPRINT plate, which was then baked at 225°F for five minutes. The plate was

1 transferred to a rotary offset press, developed, and used to print black ink on standard copy paper
2 stock. The fluids containing MONAZOLINE C, O and T all produced good images in excess of
3 100 impressions.

4

5 EXAMPLE 21

6 A marking fluid was mixed with the following components: 87 g distilled water, 1 g
7 MONAZOLINE C, 5 g butyldiglycol, and 7 g glycerine. An image was jetted down onto a KPG
8 DIRECTPRINT plate, which was then baked at 230°F for three minutes. The plate was
9 transferred to a rotary offset press, developed, and used to print black ink on standard copy paper
10 stock. Images with sharp solids and good dot definition were produced.

11

12 Proprietary Plates

13 In this aspect of the invention, it is not necessary to use a commercially available or
14 presensitized plate. Instead, the only requirement is that the plate has a press-worthy oleophilic
15 coating that is soluble to a developer and that a jettable insolubilizing fluid can be developed for
16 it.

17 Similar to the embodiment of the invention above described in which positive plates
18 comprised of quinone diazide sulfonic acid esters and alkali soluble resins are blanket exposed
19 producing carboxylic acids which are then decarboxylated by imagewise application of an
20 insolubilizing fluid according to the invention, it is possible to make a proprietary plate coating
21 comprised of decarboxylatable carboxylic acids and alkali soluble resins but without any
22 expensive o-quinone diazides. Such a coating should have all the desirable features of the

1 positive plates according to the embodiment abovedescribed, but would not be photosensitive
2 and would also have a very long, even unlimited, shelf life. There would also be no need for the
3 abovedescribed blanket exposure step, and because o-quinone diazides are not present, the
4 heating step can be performed at a higher temperature than is possible with commercial positive
5 plates.

6 The decarboxylation reaction is represented by:



8 The reaction is favored if R contains electron withdrawing groups, three membered rings
9 adjacent to the carboxyl group and beta, gamma double bonds, and is catalyzed by both acids and
10 bases which can be incorporated in an insolubilizing fluid applied imagewise. Illustrative of the
11 compounds that undergo decarboxylation are depicted in Structures 1 – 12. The compounds
12 depicted in Structures 11 and 12 are formed by photodecomposition of their corresponding
13 napthoquinone-1,2-(diazide-2)-sulfonic acid esters which are depicted respectively in Structures
14 13 and 14.

15 The following non-limiting example serves to further illustrate this aspect of the
16 invention.

17

18 EXAMPLE 22

19 Plate Coating

20 Prepare a solution of:

1 ALNOVAL PN-430 3.2g
2 2-Benzoylbenzoic acid 2.1g
3 (from Aldrich)
4 Victoria Blue Dye 0.06g
5 Sudan M Yellow 150 0.06g
6 Ethyl Lactate 33g
7 Which is coated onto a grained, anodized, and silicated aluminum sheet using a #10 wire wound
8 rod followed by drying with a hot air dryer.

9 Insolubilizing Fluid Candidates

10 Prepare solutions A – E as follows:

		A	B	C	D	E
11						
12	Isopropyl alcohol	--	2.5g	0.5g	--	--
13	2-Isopropoxyethanol	--	2.5g	5.0g	--	--
14	Water	80g	45g	33g	45g	49g
15	Sulfuric Acid, 96%	20g	5g	1g	--	--
16	2-Hydroxy-4-methoxy-					
17	benzophenone-5-sulfonic acid	--	--	--	5g	1.25g
18	(from Syntase)					
19	SURFYNOL 465	--	--	--	1drop	1drop

20 Drop of solutions A – E were applied onto the coated plate. The plate was then heated at
21 145°C for 4 minutes. Upon development with a dilute aqueous solution similar to that described
22 in Example 1, satisfactory images were produced.

1 If the coating of this example contained typical o-quinone diazides, it would not be
2 possible to heat the plate to 145°C for a substantial period without fogging (thermally
3 insolubilizing) the plate. Thus a process for chemical insolubilization of a non-photosensitive
4 coating following by a heating step presents unique and surprising advantages.

5 In another aspect of the invention, it is well known in the art that amines can act as epoxy
6 hardeners. In an embodiment of the invention abovedescribed it is taught how to make a jettable,
7 stable fluid with effective amine hardeners such as the ANCAMIDES and polyethylenimines.
8 Thus according to another aspect of the present invention, it is possible to use such an
9 insolubilizing fluid in conjunction with a plate coating comprised of epoxy monomers.

10 The following non-limiting example serves to further illustrate the invention.

11

12 **EXAMPLE 23**

13 1 g of EPON 1031, 8 g of methylcellosolve, and 3 g isopropyl alcohol were mixed and
14 heated to make a clear solution. EPON 1031 is a multifunctional
15 epichlorohydrin/tetraphenolethane epoxy resin from Shell Chemicals. The solution was coated
16 onto silicated aluminum plate to create an epoxy emulsion coating.

17 1% (by weight) aqueous polyethylenimine (Mn = 10,000; Mw = 25,000) was applied to
18 this emulsion with a pipet in drops. The plate was then heated to 230°F for one minute and
19 developed with SD-100 developer (Precision Lithograining), producing an image of the dots that
20 is believed to be due to the cross linking of the epoxy by the polyethylenimine. Similarly it is
21 known that polyamines and polyamine-functionalized compounds can be effective in directly
22 cross linking resins comprising acid anhydrides or isocyanates.

1 In another aspect of the invention, it is possible to incorporate imagewise chemical
2 insolubilization into a computer-to-press system. The essential elements of the press in this
3 embodiment of the invention are shown in Fig. 5. A conventional offset lithographic press has
4 dampening rollers 60 and inking rollers 64, which in normal operation, supply water-based
5 dampening fluid 62 and ink 66 to a printing plate mounted on a plate cylinder 68. In normal
6 printing operation, ink in the form of the image on the plate is transferred to the blanket cylinder
7 70 and then to the paper that is conveyed through the press via the impression cylinder 72. In
8 this embodiment, an unimaged on-press developable plate is mounted on the plate cylinder 68. It
9 is then imaged with an insolubilizing fluid using an ink jet printhead 74 aligned to the plate
10 cylinder 68. After imaging, if necessary to complete the insolubilization reaction, the plate can
11 be heated in situ (not illustrated). Then the plate can be developed using the working fluids of
12 the press and used in normal printing operation as above-described.

13 The foregoing is exemplary and not intended to limit the scope of the claims that follow.

14